

REMARKS/ARGUMENTS

A Second Preliminary Amendment has been filed which amends the term "multilaminar" to "multilayer". It is understood that the relevant Russian word may be translated as either multilaminar or multilayer; however, in the context of the present application, the term "multilayer" is preferred. As for amending the term "hard alloy" to also include in parenthesis "cemented carbide", the term "hard alloy" is a well known expression in the art among many scientists, and a further equivalent expression among scientists is also the term "cemented carbide".

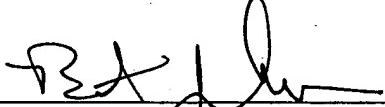
It is respectfully requested that the Examiner enter the foregoing Second Preliminary Amendment prior to a first Office Action on the merits of the application.

Attached hereto is a marked up version of the changes made to the specification and claims by the current amendment. The attached page is captioned "Version With Markings to Show Changes Made."

Respectfully submitted,

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VERSION WITH MARKINGS TO SHOW CHANGES MADE

In the Specification:

Paragraph beginning at line 6 of page 4 has been amended as follows:

EP 0 411 646 A1 describes a [multilaminar]multilayer coating containing alternating layers of tungsten and a mixture of tungsten with tungsten carbides in the form of W₂C, W₃C or a mixture of them. It is demonstrated that such a coating increases the resistance of the material to wear and erosion. It is known, however, that the maximum composition effect is observed for layers with a distinct boundary between them. This is obviously not the case for the conjunction of layers of tungsten and the mixture of tungsten with tungsten carbide which is characteristic of this patent.

Paragraph beginning at line 11 of page 8 has been amended as follows:

By using the proposed invention and also the described new method of coating deposition, one can also obtain [multilaminar]multilayer coatings with alternating layers of tungsten and layers containing tungsten carbides alloyed with fluorine and possibly with fluorocarbon compositions, including mixtures of these carbides with each other and with tungsten or carbon. The ratio of thicknesses of the alternating layers ranges from 1:1 to 1:5.

Paragraph beginning at line 18 of page 8 has been amended as follows:

The construction material itself, with a bilaminar or [multilaminar]multilayer coating deposited in accordance with the proposed method, is also an object of this invention.

Paragraph beginning at line 1 of page 9 has been amended as follows:

The examples given illustrate the production of complex coatings in which the layer of coating containing this or that tungsten carbide or mixtures of the carbides with each other and with tungsten and carbon is superimposed on a tungsten layer previously deposited on the substrate. The examples cover bilaminar coatings (internal layer of tungsten and external layer containing one or more tungsten carbides), and [multilaminar]multilayer coatings with alternating layers of tungsten and layers containing tungsten carbides.

Paragraph beginning at line 9 of page 9 has been amended as follows:

The construction material on which the composite coating is deposited (or its external layer relative to the coating, in the case of bimetal) contains one of the following base materials: hard alloys (cemented carbide), ceramics such as silicon carbide, silicon nitride, aluminium oxide, zirconium oxide, carbon-carbon composition materials etc., several iron-containing alloys such

as iron, carbon steels, stainless steels, tool and high-speed steels and cast iron, or other materials from the following list: copper, silver, gold, cobalt, nickel, rhodium, rhenium, platinum, iridium, silicon, tantalum, niobium, vanadium, tungsten, molybdenum, carbon, nitrogen, boron, their alloys, compounds and mixtures, and also titanium alloys. The construction material or its outer layer adjacent to the coating should preferably consist of alloys with a nickel content exceeding 25 wt% e.g. Invar, Nichrome, Monel etc.

Paragraph beginning at line 21 of page 9 has been amended as follows:

In the case of deposition onto chemically active materials such as iron, carbon steels, stainless steels, tool and high-speed steels, cast iron, titanium alloys and hard alloys (cemented carbide) containing titanium, it is preferable to deposit intermediate coatings containing materials chemically resistant to hydrogen fluoride, from the following list: copper, silver, gold, cobalt, nickel, rhodium, rhenium, platinum, iridium, tantalum, molybdenum, niobium, vanadium and boron. An intermediate coating of thickness 0.5-20 µm is deposited by electrochemical or chemical deposition from aqueous solutions, melt electrolysis, chemical or physical vapour deposition (e.g. by means of magnetron spraying) or by other methods.

Paragraph beginning at line 14 of page 10 has been amended as follows:

The substrates, degreased and free of contaminations, are put inside a direct-flow chemical reactor with an electric heater. The chemical reactor is evacuated by means of a roughing pump with a liquid nitrogen freezing trap up to maximum vacuum, after which hydrogen or argon is supplied to the reactor. The reactor with the items in it is then heated to the required temperature, which is maintained for 0.5-1 hours. After this, the required hydrogen flow rate and total pressure in the reactor are set. The required flow rate of tungsten hexafluoride, heated beforehand to 30°C, is then set. After the retention of the items in the set conditions for the time necessary for the application of the internal tungsten layer, the required total pressure is set and a certain flow rate of the carbon-containing gas (e.g. propane), previously heated to the required temperature, into the reaction mixture is set. A [multilaminar]multilayer composition coating is obtained by repeating the operation. After that, the supply of gas is terminated and the substrates are kept at constant temperature for 0.5-1 hours. After this stage, the temperature of the reactor is decreased to room temperature with hydrogen or argon being continuously supplied. The supply of hydrogen or argon is then terminated, the reactor is evacuated to maximum vacuum, and air is then admitted to it. The substrates with composite coatings are then removed from the reactor. Specific examples of the described method of deposition of a composite coating are described below. The tests for hardness and for determining the phase composition of the coating were carried out in the following manner.

Paragraph beginning at line 6 of page 11 has been amended as follows:

Hardness tests were conducted using a PMT-3 instrument. Samples made from steel or hard alloys (cemented carbide) with the composite coating applied were cut across. The cut was then ground with emery cloth and polished with diamond paste to maximum smoothness. The microhardness of the coatings was determined by pressing the pyramid-shaped diamond micro-indenter of the PMT-3 instrument into the middle of the external or internal layer of the composite coating at the polished cross-cut of the sample. The results were averaged over 7-10 measurements. It was determined from them that the microhardness of the internal tungsten layer was 350-600 kG/mm², the microhardness of tungsten monocarbide (WC) was 1900 kG/mm², the microhardness of tungsten semicarbide (W₂C) was 3000 kG/mm² and the microhardness of tungsten subcarbide W₃C was 3100 kG/mm². The new tungsten subcarbide W₁₂C possesses the greatest microhardness – 3500 kG/mm². Mixtures of tungsten carbides have intermediate hardness values.

Paragraph beginning at line 20 of page 11 has been amended as follows:

[Multilaminar] Multilayer coatings possessed medium hardness. In this case, the force on the diamond pyramid was selected so that the imprint extended into not less than four layers of the [multilaminar] multilayer coating. These hardness measurements were also repeated 7-10 times.

Paragraph beginning at line 25 of page 13 has been amended as follows:

A sample made from hard alloy (cemented carbide) VK-10 is retained in the reaction chamber at temperature 650°C in a medium of tungsten hexafluoride (WF₆) and hydrogen (H₂) at ratio 0.08 for 1 min and then in a medium of WF₆, H₂ and propane (C₃H₈) at a ratio of WF₆ to H₂ equal to 0.08 and a ratio of C₃H₈ to H₂ equal to 0.95 for 80 min; the C₃H₈ is thermally activated beforehand at 730°C and the reaction mixture pressure is 8.8 kPa.

Paragraph beginning at line 1 of page 14 has been amended as follows:

The construction material thus obtained with hard alloy (cemented carbide) VK-10 as the base material has a composite coating with an internal tungsten (W) layer of thickness 0.7 µm and an external layer (mixture of W₂C and WC) of thickness 32 µm. The microhardness of the coating is 2800 kG/mm².

Paragraph beginning at line 4 of page 19 has been amended as follows:

A sample made from hard alloy (cemented carbide) VK6 is retained in the reaction chamber at temperature 620°C (a) in a mixture of tungsten hexafluoride (WF₆) and hydrogen (H₂) at ratio 0.08 for 2 min and then (b) in a medium of WF₆, H₂ and propane (C₃H₈) at a ratio of WF₆ to H₂

equal to 0.08 and a ratio of C₃H₈ to H₂ equal to 1.5 for 16 min; the C₃H₈ is thermally activated beforehand at 750°C and the reaction mixture pressure is 5.2 kPa. Operations (a) and (b) are repeated four times in succession. The fluorine content in the [multilaminar]multilayer coating is 9·10⁻³ wt%.

Paragraph beginning at line 12 of page 19 has been amended as follows:

The construction material thus obtained with hard alloy (cemented carbide) VK6 as the base material has a composite coating with four alternating layers of W with thickness 3.0 µm and of WC with thickness 7.0 µm at a ratio of thicknesses 1:2.3 and total thickness of the composite coating 40 µm. The average microhardness of the coating is 1320 kG/mm².

Paragraph beginning at line 20 of page 19 has been amended as follows:

A sample made from hard alloy (cemented carbide) VK10 is retained in the reaction chamber at temperature 650°C (a) in a mixture of tungsten hexafluoride (WF₆) and hydrogen (H₂) at ratio 0.08 for 1 min and then (b) in a medium of WF₆, H₂ and propane (C₃H₈) at a ratio of WF₆ to H₂ equal to 0.08 and a ratio of C₃H₈ to H₂ equal to 0.95 for 80 min; the C₃H₈ is thermally activated beforehand at 730°C and the reaction mixture pressure is 8.8 kPa. Operations (a) and (b) are repeated four times in succession.

Paragraph beginning at line 27 of page 19 has been amended as follows:

The construction material thus obtained with hard alloy (cemented carbide) VK10 as the base material has a composite coating with four alternating layers of W with thickness 0.7 µm and of a mixture of WC and W₂C with thickness 32 µm at a ratio of thicknesses 1:45.7 and total thickness of the composite coating 130.8 µm. The average microhardness of the coating is 2200 kG/mm².

Paragraph beginning at line 30 of page 24 has been amended as follows:

The invention can be used for strengthening tools made from steel, hard alloy (cemented carbide) or diamond which are used for processing materials by means of cutting or pressing. The latter is the most promising field for applications of the proposed technology due to the absence of competing coating technologies applicable to the manufacture of press tools of complex shape for drawing wires and tubes and for extruding profile sections from aluminium, copper, steel and other metals and alloys. The carbon-tungsten coatings referred to can be deposited on tools and casting moulds used for moulding items from plastics, silicate masses and other abrasive mixtures.

In the Claims:

Claims 33, 67-70, 72, 76, and 81 have been amended as follows:

33. (Twice Amended) Process in accordance with claim 31, characterized in that, before the application of a coating to materials or items made from materials selected from a group including iron, carbon steels, stainless steels, cast irons, titanium alloys and hard alloys (cemented carbide) containing titanium, a coating is applied to them consisting of materials which are chemically resistant to hydrogen fluoride, namely nickel, cobalt, copper, silver, gold, platinum, iridium, tantalum, molybdenum and alloys, compounds and mixtures of these, by electrochemical or chemical deposition from aqueous solutions, electrolysis of melts or physical and chemical vapor deposition.

67. (Twice Amended) [Multilaminar]Multilayer coating made from alternating layers of tungsten and layers containing tungsten carbide in accordance with claim 1.

68. (Amended) [Multilaminar]Multilayer coating made from alternating layers of tungsten and layers containing tungsten carbide in accordance with claim 7.

69. (Twice Amended) [Multilaminar]Multilayer coating in accordance with claim 67, characterized in that the thickness of its individual layers ranges from 2 to 10 μm and the ratio of the thicknesses of the alternating layers ranges from 1:1 to 1:5.

70. (Twice Amended) Process for the deposition of [multilaminar]multilayer coatings on substrates, preferably on construction materials and items made from them, consisting of alternating layers of tungsten and layers containing tungsten carbide or mixtures of tungsten carbides with each other, with tungsten or with free carbon, said process to include the following stages:

(a) placing the substrate in a chemical vapor deposition reactor;
(b) evacuating the reactor;
(c) heating the said substrate;
(d) supplying tungsten hexafluoride and hydrogen to the reactor;
(e) retaining the substrate in the said gaseous medium for the time interval necessary for the formation of the tungsten layer on the substrate;

(f) in addition to the said tungsten hexafluoride and hydrogen, supplying a previously thermally activated carbon-containing gas to the reactor;

(g) retaining the substrate in the gaseous medium formed at stage (f) for the time necessary for the formation of the outer layer containing tungsten carbide or mixtures of tungsten carbides with each other, with tungsten and with free carbon; stages (d) to (g) are repeated several times in order to form alternating layers of tungsten and layers containing tungsten carbides.

72. (Twice Amended) Process in accordance with claim 70, characterized in that, before the application of a coating to materials or items made from materials selected from a group including iron, carbon steels, stainless steels, cast irons, titanium alloys and hard alloys (cemented carbide) containing titanium, a coating is applied to them consisting of materials

which are chemically resistant to hydrogen fluoride, namely nickel, cobalt, copper, silver, gold, platinum, iridium, tantalum, molybdenum and alloys, compounds and mixtures of these, by electrochemical or chemical deposition from aqueous solutions, electrolysis of melts or physical and chemical vapor deposition.

76. (Amended) Construction material comprising a substrate and a [multilaminar]multilayer coating consisting of alternating layers of tungsten and layers containing tungsten carbide alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt% and possibly with fluorocarbon compositions with carbon content up to 15 wt% and fluorine content up to 0.5 wt%.

81. (Amended) Construction material comprising a substrate and a [multilaminar]multilayer coating consisting of alternating layers of tungsten and layers containing a mixture of at least two tungsten carbides alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt% and possibly with fluorocarbon compositions with carbon content up to 15 wt% and fluoride content up to 0.5 wt%.